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(56) Documents cited

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(58) Field of search

G2J

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(54) Sample carrier for flameless atomic-absorption and emission spectroscopy

(57) The sample carrier consists of expanded graphite cold-rolled or cold-pressed at high pressure. It is preferably made by deep-drawing from commercially available graphite foil. The sample carrier may be coated with pyrolytic graphite after forming to seal the surface and provide additional mechanical strength.

In order to avoid damage to the foil during the deep-drawing process the graphite foil may be prior coated with a stabilising film comprising a soluble deformable polymer material. This material is preferably volatile at the preheating temperatures applied to the sample holder prior to the coating with pyrolytic graphite as this eliminates the necessity for a separate step to remove the film.

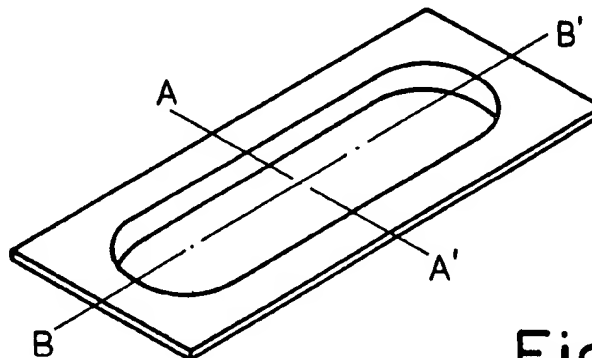


Fig.2

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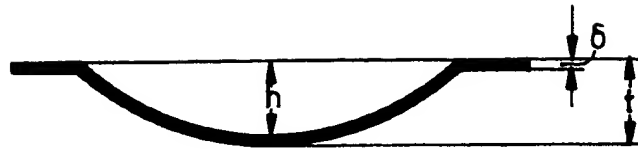


Fig. 1

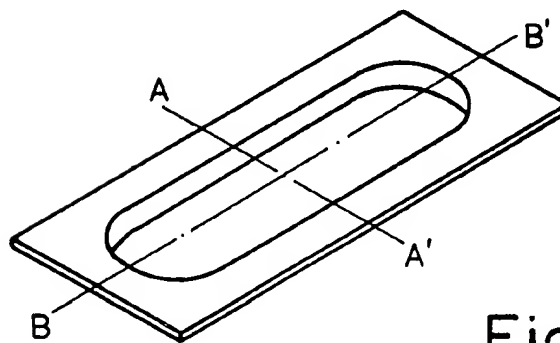


Fig. 2



Fig. 2a

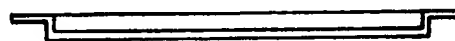


Fig. 2b

SPECIFICATION

Sample carrier for flameless atomic-absorption and atomic-emission spectroscopy and method of manufacturing the same

The invention relates to a sample carrier for flameless atomic-absorption and atomic-emission spectroscopy (AAS/AES) and to a method of manufacturing the same.

In flameless AAS and AES with electro-thermal atomisation a cuvette, in most cases a graphite tube, is employed which has a double function. On the one hand it serves as a holder of the sample and on the other hand it serves as a resistance element i.e. as a furnace for the electric heating. The sample to be analysed is, in general, dissolved and at the beginning of the analysis a few μl of this solution are injected into an opening (filling opening) in the side of the cuvette. Then in accordance with a given temperature-time programme the cuvette is heated to different temperatures up to the atomizing temperature, which may attain 3000°C depending on the element assumed to be present, and subsequently cooled.

The following effects, which adversely affect the performance and the result of the analysis, may occur in the direct injection of the sample solution into the tube. Residues of a sample may be retained due to the penetration of sample substance into the cuvette wall. Under given conditions these residues affect the result of further analysis carried out with the cuvette (so-called memory effect). Due to wetting processes some of the sample may spread along greater and more remote regions of the cuvette inner wall and thus get lost for the analysis. There is always a certain interaction between the sample and the cuvette wall, which finally reduces the lifetime of the cuvette.

A technique of sample introduction in which a direct contact between sample substance and the cuvette wall is avoided is known from Spectrochim. Acta 35B (1980) 701. This is achieved by using small, separate containers which are introduced in the cuvette. Such containers, when used as sample carriers, are termed "platforms", "inserts" or "sample holders". Heating of the sample carriers preferably occurs by radiation from the cuvette wall and to a lesser extent also by heat conduction. In view of the extremely high temperature of up to 3200°K used in AAS/-AES, the sample carriers have to be made from correspondingly temperature-resistant materials. On the other hand the time taken to raise the temperature of the sample to the required temperature should be as short as possible. This implies the requirement that the mass of the sample carrier should be as small as possible commensurate with mechanical stability. A further necessity for making the

sample carrier as small (flat) as possible results from the fact that the carrier introduced into the cuvette should obstruct the measuring radiation or affect it in some other way to the minimum possible extent.

The volumes of the sample to be inserted are typically—in accordance with the system—from a few μl up to about $100\mu\text{l}$. The sample to be analysed can, as usual, be injected into the sample carrier which is already arranged in place or the sample carrier may be filled outside the cuvette and subsequently be introduced into the cuvette operating as the atomizing device. The latter can not be avoided when the sample is not dissolved in an acid or in another solvent, but it is to be introduced directly as a solid (for example, a metal or a mineral, glass or stone splitter, organic solid, animal tissue part, etc.). The solid samples usually have irregular shapes in volumes of about one up to a few mm^3 . These irregular shapes and volumes mean that an introduction through the usually very narrow dosing aperture (diameter of about 1.5 to 2.0 mm) is not possible. For the solid sample dosing technique with separate filling and subsequent introduction into the atomizing device, professionally termed "solid sampling" or "solid state sampling" the sample carrier cannot be dispensed with.

In "solid sampling" the function of the sample carrier comes down in many cases, in which the sample substance does not pass, for example during heating, through a low viscous liquid or fluid melting phase, to fixation or localisation of the sample of the cuvette. It is then possible to make the sample holder in the form of a very flat container having a useful volume of a few mm^3 to about 100 mm^3 so that the radiation can pass quite unhindered through the cuvette.

The sample carriers provided by some manufacturers consist of highly pure electrographite, which are machined into the desired shape—for example, the shape of flat, rectangular plates 1 mm thick and for example, of a size of about $5 \times 12\text{ mm}$ with a mass of about 80 to 100 mg having a milled, tub-shaped depression of, for example, 0.5 mm deep. These sample carriers involve stringent requirements in manufacture, working and finish and are, therefore, relatively expensive. Moreover, they have the disadvantage of a relatively high terminal inertia.

It is an object of the invention to enable the provision of sample carriers (inserts, platforms) which have adequate performance and which can be manufactured in a very simple manner at low cost.

The invention provides a sample carrier for flameless atomic absorption or atomic emission spectroscopy characterised in that the sample carrier is made from expanded graphite cold-rolled or cold-pressed at a high pressure.

The sample carrier may consist of graphite foil. In this case the starting material is a commercially available graphite foil, which is offered by various manufacturers ("Papyex" of le Carbone Lorraine, "Sigraflex" of Sigrif, "Grafoil" of Union Carbide) in slightly differing qualities and in different sizes. All above-mentioned products are made from pure graphite without additive by rolling expanded graphite flakes at a high pressure. The foils and tapes, which can be obtained with widths of up to 50cm and in lengths of up to 50mm, have a very smooth surface. The available thicknesses lie between about 0.1 and 0.35mm. The most conspicuous properties are the relatively low densities of about 1.0 g/cm³ and the anisotropy resulting from the fact that owing to their layer structure the graphite particles preferentially direct themselves parallel to the rolling direction under the influence of the rolling pressure.

According to statements from the manufacturers these graphite foils are particularly suitable for corrosion-resistant, heat-resistant stuffing box packing and seals, but also as furnace coatings and heat-protecting screens (in non-oxidizing atmospheres).

It has now been established that graphite foils of the kind described can be deformed in the cold state, without disturbance of the internal structure, up to a degree which is sufficient for the manufacture of small containers like the sample carrier. In particular deep-drawing has been found to be a particularly appropriate method of manufacturing sample carriers which satisfy all requirements both by their general properties and by the obtainable useful volume.

A disadvantage of the foils is their low mechanical rigidity and their resultant sensitivity to damage in handling. Also, the foils are in their normal state chemically fairly active, particularly at higher temperatures. This can be accounted for by the fact that the reactive, lattice-plane sides of the rolled graphite particles of the foils represent a high number of active centres, both at the surface and in the volume which is readily accessible due to the high porosity.

In the case of sample carriers made from foils, in which said reactivity is not expressly desired, for example as a reduction means for oxides, it is advantageous to coat the sample carrier at least partly with pyrolytic graphite, after the deep drawing process. Thus, three desirable features are obtained:

1. By heating to a deposition temperature of about 2300°K in vacuo (pressure of 10⁻³ mbar or lower) degasification of the relatively large pore volume of about 56% and purification by evaporation of any of the impurities, which become volatile under these conditions will occur.

2. The coating of pyrolytic graphite has the effect of a chemical passivation of the foil

surface and seals the inner pore volume as a strongly diffusion-inhibiting barrier.

3. The envelope of pyrolytic graphite mechanically reinforces the basic foil, which thus becomes readily handleable and insensitive to damage.

In deep-drawing the graphite foils, serving as starting material, cracks may occur when the degree of deformation exceeds a given upper limit. A further difficulty occurs when the stamper (matrix) has sharp edges as, for example, in the case of tub-like depressions of the sample carrier. In this case cracks, in particular at corners, bends and sides, are difficult to avoid.

It has been found that damage-free deformation of the graphite foils, even where sharp-edged profiles are required is possible when the graphite foil is provided with a stabilizing surface film. This may be achieved by covering the surface with a thin plastics foil. In the case of the graphite tapes preferably used for the manufacture of the sample carriers (characteristic dimensions: 20mm wide, 0.2 to 0.3mm thick, length up to 50m) for example self-adhesive tape is quite suitable. It is surprising to find how much the impressibility of the graphite tape can be improved by an adhesive tape on one side or on both sides. In coating with pyrolytic graphite subsequent to the stamping or deep-drawing process in the heating phase (up to 2100°C in vacuo) the applied tape is substantially removed by depolymerisation and evaporation.

In an alternative method the stabilizing film is applied by impregnating the graphite foil in a solution of a polymer substance. Impregnation with aqueous solutions of polyvinyl alcohol (PVA) and also aqueous solutions of (modified) methylcellulose appeared to be particularly suitable. Even a single immersion into a concentrated or a saturated aqueous solution of said kind enables the pressing of a sample carrier boat without cracks or other damage. The impregnation can be repeated several times with intermediate drying. The film of PVA or methylcellulose used for the pressing operation only is also removed in the heating phase prior to coating with pyrolytic graphite.

A further advantage of the intermediate stabilisation by means of a film of polymer substances resides in that the tensile strength and hence the handleability of the preferably tape-shaped graphite foils are markedly improved. The latter is very important for coating tape in a continuous process.

The invention provides the advantage that by cold rolling expanded graphite at high pressure or by deep-drawing commercially available graphite foils sample carriers used in AAS and AES—in particular for the so-called solid state sampling—can be manufactured in a particularly simple manner at low cost. In particular the method can be continuously

carried out since the raw material is obtainable in practically endless tapes (up to 50m). In principle, two types of sample carriers can be made: a. the uncoated, deep-drawn form, b. the form afterwards coated with pyrolytic graphite.

Form a) is mechanically less stable and is more likely to be damaged. Chemically, however, it is moderately reactive and it can have a useful reducing effect on a plurality of substances at higher temperatures.

Form b) is mechanically stronger and hence more readily handleable and it is less likely to be damaged. Compared with form a) it is chemically passive. Moreover, penetration of sample substances into the porous basic material is blocked.

The two forms have in common a very low thermal inertia. Owing to the small cost of manufacture the question of re-usability is insignificant (disposable carrier).

The deep-drawing method provides a rational manufacture at low cost, as compared with other methods such as turning, milling and sawing, for sample carriers of very small size from graphite foil. The sample carriers can be used directly or after being coated with a protective layer of pyrolytic graphite. The plastic formability of the foils is limited so that the formed body often shows damage, for example, holes and cracks. When these defects are slight, they can, in general, be covered (sealed) by the pyrolytic coating. The sensitivity to damage is considerably reduced when the graphite foil is provided, prior to deformation, with a stabilizing film of a soluble, deformable polymer material which becomes volatile at higher temperatures (when necessary in vacuo).

Embodiments of the invention will now be described, by way of example, with reference to the accompanying drawings, in which:—

Figure 1 shows a sectional view of a sample carrier having a part spherical depression,

Figure 2 is a perspective view of a boat-shaped sample carrier,

Figure 2a is a sectional view of the sample carrier of Fig. 2 taken on the line A-A', and

Figure 2b is a sectional view of the sample carrier of Fig. 2 taken on the line B-B'.

Example 1.

Graphite foils in the form of tapes of 20 and 25mm wide 0.2 and 0.3mm thick, lengths up to 15m (make Papyex N of Le Carbone Lorraine) were employed as a starting material for deep-drawing at room temperature. In pressing part spherical depressions in the form of ball caps (Fig. 1) it was found that no damage of the foil structure occurred when the ratio between deformation depth t and cap diameter D did not exceed the value $t/D = 0.1$. At values higher than 0.1 cracks or ruptures usually occur. Sample carriers with such part spherical depressions with dia-

meters of 5, 9 and 11mm were made. These diameters correspond to associated deformation depths of 0.5, 0.9 and 1.0 to 1.1mm: the depression depths h of the depressions required for calculating the "useful volumes" follow from

$$h = t - \delta (\delta = \text{foil thickness}).$$

For the above-indicated values useful volumes of the sample carriers of $V_n = 3\text{mm}^3$, 22mm^3 and 38mm^3 were calculated. By means of a simple deep-drawing device sample carriers with part spherical depressions were very rapidly and very reproducibly made to volumes of $V_n = 10\text{mm}^3$ and 20mm^3 . The weights of such sample carriers are about 20 to 35mg.

Sealing of the sample carriers was carried out by known methods of hot-gas pyrolysis. The thickness of the applied pyrographite coatings can be varied according to requirements within wide limits and is preferably between 1 and $100\mu\text{m}$.

Example 2.

A tape-shaped graphite foil having a width of 20mm and a thickness of 0.2mm was dipped once at room temperature (20°C) into a saturated, aqueous solution of PVA and dried. By assessing the weight, the thickness of the resultant surface film was found to be about $2\mu\text{m}$. This film thickness is sufficient for crack-free stamping of a tub-like depression of 3mm wide and 0.5mm deep with sharp edges ($R = 0.5\text{mm}$), wherein R is the inner radius of curvature of the edges concerned. By several repetitions of the immersion PVA films (coatings) of 20 to $30\mu\text{m}$ were obtained.

By dipping ten times into a saturation solution of methylcellulose layers of $45\mu\text{m}$ thickness were produced. In subsequent coating by the CVD method at 2000°C in C_3H_8 at a pressure of 2.0mbar for one hour the "boat" of Fig. 2 was covered by a dense, corrosion-resistant layer of pyrolytic graphite. This sample carrier then has a weight of about 30mg.

CLAIMS

1. A sample carrier for flameless atomic absorption and atomic emission spectroscopy, characterised in that the sample carrier is made from expanded graphite cold-rolled or cold-pressed at a high pressure.
2. A sample carrier as claimed in Claim 1, characterised in that it is made from graphite foil.
3. A sample carrier as claimed in Claim 2, characterised in that it is made from deep-drawn graphite foil.
4. A sample carrier as claimed in Claim 2 and 3, characterised in that it is coated at least partly with pyrolytic graphite.
5. A method of manufacturing a sample carrier for flameless atomic absorption and atomic emission spectroscopy comprising cold

rolling or cold pressing expanded graphite at high pressure.

6. A method as claimed in Claim 5, in which the expanded graphite is in the form of graphite foil and in which prior to pressing or rolling the graphite foil is provided with a stabilising film on the surfaces to be deformed.

7. A method as claimed in Claim 6, in which the stabilising film is a soluble, deformable polymer material which is volatile at temperatures below 2100°C.

8. A method as claimed in Claim 6 or Claim 7, in which the stabilising film is an adhesive tape which is applied to the surfaces of the foil to be deformed.

9. A method as claimed in Claim 6 or Claim 7, in which the stabilising film is applied to the foil by immersing the foil in a solution of the polymer material.

10. A method as claimed in any of Claims 5 to 9, in which the formed expanded graphite is coated over at least part of its surface with pyrolytic graphite.

11. A sample carrier for flameless atomic absorption or atomic emission spectroscopy substantially as described herein with reference to the accompanying drawings.

12. A method of manufacturing a sample carrier for flameless atomic absorption or atomic emission spectroscopy substantially as described herein with reference to the accompanying drawings.

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